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(54) Aromatics saturation process for diesel boiling-range hydrocarbons.

(57) In a process for the concomitant hydrogenation of aromatics and sulphur-bearing hydrocarbons in an aromatics- and sulphur-bearing, diesel boiling-range hydrocarbon feedstock, the feedstock is contacted at a temperature between 315 and 399 °C and a pressure between 40 and 168 bar in the presence of added hydrogen with a first catalyst bed containing a hydrotreating catalyst containing nickel, tungsten and optionally phosphorous supported on an alumina support, and, after contact with the first catalyst bed, the hydrogen and feedstock without modification, is passed from the first catalyst bed to a second catalyst bed where it is contacted at a temperature between 315 and 399 °C and a pressure between 40 and 168 bar with a hydrotreating catalyst containing cobalt and/or nickel, molybdenum and optionally phosphorous supported on an alumina support.

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This invention relates to a hydrotreating process for the saturation of aromatics in diesel boiling-range hydrocarbon feedstocks.

Environmental regulations are requiring that the aromatics and sulphur content of diesel fuels be reduced. Reduction of the aromatics and sulphur content will result in less particulate and sulphur dioxide emissions from the burning of diesel fuels. Unfortunately, a hydrotreating catalyst that is optimized for hydrodesulphurization will not be optimized for aromatics saturation and vice versa. A "stacked" or multiple bed hydrotreating system has been developed comprising a Ni-W/alumina catalyst "stacked" on top of a Co and/or Ni-Mo/alumina catalyst which offers both cost and activity advantages over the individual catalysts for combined hydrodesulphurization and aromatics saturation.

The present invention comprises a process for the concomitant hydrogenation of aromatics and sulphur-bearing hydrocarbons in an aromatics- and sulphur-bearing hydrocarbon feedstock having substantially all of its components boiling in the range of 93 to 482 °C which process comprises:

(a) contacting at a temperature between 315 and 399 °C and a pressure between 40 and 168 bar in the presence of added hydrogen said feedstock with a first catalyst bed containing a hydrotreating catalyst comprising nickel, tungsten and optionally phosphorous supported on an alumina support, and

(b) passing the hydrogen and feedstock without modification, from the first catalyst bed to a second catalyst bed where it is contacted at a temperature between 315 and 399 °C and a pressure between 40 and 168 bar with a hydrotreating catalyst comprising cobalt and/or nickel, molybdenum and optionally phosphorous supported on an alumina support.

The present process is particularly suited for hydrotreating feedstocks containing from 0.01 to 2 percent by weight of sulphur. For sulphur-deficient feedstocks, sulphur-containing compounds may be added to the feedstock to provide a sulphur level of 0.01-2 percent by weight.

The dual catalyst bed process of the present invention provides for better aromatics saturation at lower hydrogen partial pressures than does a process utilizing only one of the catalysts utilized in the dual bed system.

The present invention relates to a process for reducing the sulphur and aromatics content of a diesel boiling-range hydrocarbon feedstock by contacting the feedstock in the presence of added hydrogen with a two bed catalyst system at hydrotreating conditions, i.e., at conditions of temperature and pressure and amounts of added hydrogen such that significant quantities of aromatics are saturated and significant quantities of sulphur are removed from the feedstock. Nitrogen-containing impurities, when present, are also significantly reduced.

The feedstock to be utilized is a diesel boiling-range hydrocarbon feedstock having substantially all, that is, greater than 90 percent by weight, of its components boiling between 93 and 482 °C, preferably between 121 and 427 °C and more preferably between 149 and 399 °C and which suitably contains from 0.01 to 2, preferably from 0.05 to 1.5 percent by weight of sulphur present as organosulphur compounds. Feedstocks with very low or very high sulphur contents are generally not suitable for processing in the present process. Feedstocks with very high sulphur contents can be subjected to a separate hydrodesulphurization process in order to reduce their sulphur contents to 0.01-2, preferably 0.05-1.5 percent by weight prior to being processed by the present process. Feedstocks with very low sulphur contents can be adjusted to sulphur levels of 0.01-2, preferably 0.05-1.5 percent by weight by the addition of suitable amounts of sulphur containing compounds. Suitable compounds include, for example, the mercaptans, particularly the alkyl mercaptans; sulphides and disulphides such as, for example, carbon disulphide, dimethyl sulphide, dimethyldisulphide, etc.; thiophenic compounds such as methyl thiophene, benzothiophene, etc., and polysulphides of the general formula $R-S_{(n)}-R'$. There are numerous other sulphur-containing materials that can be utilized to adjust the sulphur content of the feedstock. U.S. patent no. 3,366,684, lists a number of suitable sulphur-containing compounds.

The present process utilizes two catalyst beds in series. The first catalyst bed is made up of a hydrotreating catalyst comprising nickel, tungsten and optionally phosphorous supported on an alumina support and the second catalyst bed is made up of a hydro-treating catalyst comprising a hydrogenating metal component selected from cobalt, nickel and mixtures thereof, molybdenum and optionally phosphorous supported on an alumina support. The term "first" as used herein refers to the first bed with which the feedstock is contacted and "second" refers to the bed with which the feedstock, after passing through the first bed, is next contacted. The two catalyst beds may be distributed through two or more reactors, or, in the preferred embodiment, they are contained in one reactor. In general the reactor(s) used in the present process is used in the trickle phase mode of operation, that is, feedstock and hydrogen are fed to the top of the reactor and the feedstock trickles down through the catalyst bed primarily under the influence of gravity. Whether one or more reactors are utilized, the feedstock with added hydrogen is fed to the first catalyst bed and the feedstock as it exits from the first catalyst bed is passed directly to the second catalyst bed without

modification. "Without modification" means that no sidestreams of hydrocarbon materials are removed from or added to the stream passing between the two catalyst beds. Hydrogen may be added at more than one position in the reactor(s) in order to maintain control of the temperature. When both beds are contained in one reactor, the first bed is also referred to as the "top" bed.

5 The volume ratio of the first catalyst bed to the second catalyst bed is primarily determined by a cost effectiveness analysis and the sulphur content of the feed to be processed. The cost of the first bed catalyst which contains more expensive tungsten is approximately two to three times the cost of the second bed catalyst which contains less expensive molybdenum. The optimum volume ratio will depend on the particular feedstock sulphur content and will be optimized to provide minimum overall catalyst cost and
10 maximum aromatics saturation. In general terms the volume ratio of the first catalyst bed to the second catalyst bed will range from 1:4 to 4:1, more preferably from 1:3 to 3:1, and most preferably from 1:2 to 2:1.

The catalyst utilized in the first bed comprises nickel, tungsten and 0-5% wt phosphorous (measured as the element) supported on a porous alumina support preferably comprising gamma alumina. It contains
15 from 1 to 5, preferably from 2 to 4 percent by weight of nickel (measured as the metal); from 15 to 35, preferably from 20 to 30 percent by weight of tungsten (measured as the metal) and, when present, preferably from 1 to 5, more preferably from 2 to 4 percent by weight of phosphorous (measured as the element), all per total weight of the catalyst. It will have a surface area, as measured by the B.E.T. method (Brunauer et al, J. Am. Chem. Soc., 60, 309-16 (1938)) of greater than 100 m²/g and a water pore volume between 0.2 and 0.6 cc/g, preferably between 0.3 and 0.5.

20 The catalyst utilized in the second bed comprises a hydrogenating metal component selected from cobalt, nickel and mixtures thereof, molybdenum and 0-5% wt phosphorous (measured as the element) supported on a porous alumina support preferably comprising gamma alumina. It contains from 1 to 5, preferably from 2 to 4 percent by weight of hydrogenating metal component (measured as the metal); from 8 to 20, preferably from 12 to 16 percent by weight of molybdenum (measured as the metal) and, when
25 present, preferably from 1 to 5, more preferably from 2 to 4 percent by weight of phosphorous (measured as the element), all per total weight of the catalyst. It will have a surface area, as measured by the B.E.T. method (Brunauer et al, J. Am. Chem. Soc., 60, 309-16 (1938)) of greater than 120 m²/g and a water pore volume between 0.2 and 0.6 cc/g, preferably between 0.3 and 0.5. Cobalt and nickel are known in the art to be substantial equivalents in molybdenum-containing hydrotreating catalysts.

30 The catalyst utilized in both beds of the present process are catalysts that are known in the hydrocarbon hydroprocessing art. These catalysts are made in a conventional fashion as described in the prior art. For example, porous alumina pellets can be impregnated with solution(s) containing cobalt, nickel, tungsten or molybdenum and phosphorous compounds, the pellets subsequently dried and calcined at elevated temperatures. Alternately, one or more of the components can be incorporated into an alumina
35 powder by mulling, the mulled powder formed into pellets and calcined at elevated temperature. Combinations of impregnation and mulling can be utilized. Other suitable methods can be found in the prior art. Non-limiting examples of catalyst preparative techniques can be found in U.S. patent no. 4,530,911 and U.S. patent no. 4,520,128. The catalysts are typically formed into various sizes and shapes. They may be suitably shaped into particles, chunks, pieces, pellets, rings, spheres, wagon wheels, and polylobes, such as
40 bilobes, trilobes and tetralobes.

The two above-described catalysts are normally presulphided prior to use. Typically, the catalysts are presulphided by heating in H₂S/H₂ atmosphere at elevated temperatures. For example, a suitable presulphiding regimen comprises heating the catalysts in a hydrogen sulphide/hydrogen atmosphere (5 %v H₂S/95 %v H₂) for about two hours at 371 °C. Other methods are also suitable for presulphiding and
45 generally comprise heating the catalysts to elevated temperatures (e.g., 204-399 °C) in the presence of hydrogen and a sulphur-containing material.

The hydrogenation process of the present invention is effected at a temperature between 315 and 399 °C, preferably between 327 and 399 °C under pressures above 39 bar. The total pressure will typically range from 41 to 169 bar. The hydrogen partial pressure will typically range from 35 to 149 bar. The
50 hydrogen feed rate will typically range from 178 to 891 vol/vol. The feedstock rate will typically have a liquid hourly space velocity ("LHSV") ranging from 0.1 to 5, preferably from 0.2 to 3.

The invention will be described by the following examples which are provided for illustrative purposes and are not to be construed as limiting the invention.

The catalysts used to illustrate the present invention are given in Table 1 below.

TABLE 1: HYDROGENATION CATALYSTS

	<u>CATALYST A</u>	<u>CATALYST B</u>
<u>Metals, Wt. %</u>		
5 Ni	2.99	2.58
W	25.81	-0-
Mo	-0-	14.12
10 P	2.60	2.93
Support	gamma alumina	gamma alumina
Surface Area, m ² /g	133	164
15 Water Pore Vol., ml/g	0.39	0.44

The feedstock utilized to illustrate the present invention is detailed in Table 2 below.

TABLE 2: PROPERTIES OF FEEDSTOCKPhysical Properties

Density, 15 °C	0.8925
API	27.04
Refractive Index, 20°C	1.4947
Pour Point	-15 °C
Flash Point	91 °C
Cetane Index (ASTM 976-80)	38.6

Elemental Content

Hydrogen	12.0 wt.%
Carbon	87.7 wt.%
Oxygen	520 ppm
Nitrogen	148 ppm
Sulphur	400 ppm ✓

Aromatic Content

FIA (ASTM 1319-84)	59.8 vol.%
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Boiling Point Distribution

<u>ASTM D-86</u>			<u>ASTM D-2887</u>		
	IBP	200 °C		IBP	173 °C
5.0 VOL.%		223	5.0 WT.%		209
10.0		242	10.0		228
20.0		254	20.0		250
30.0		266	30.0		267
40.0		277	40.0		284
50.0		288	50.0		300
60.0		300	60.0		314
70.0		312	70.0		329
80.0		325	80.0		345
90.0		344	90.0		367
FBP		364	FBP(99.5%)		416

To illustrate the present invention and to perform comparative tests, a vertical micro-reactor was used to hydrotreat the feedstock noted in Table 2. Three types of catalyst configurations were tested utilizing the catalysts noted in Table 1: a) 40 cc of Catalyst A diluted with 40 cc of 60/80 mesh silicon carbide particles, b) 40 cc of Catalyst B diluted with 40 cc of 60/80 mesh silicon carbide particles and c) 20 cc of Catalyst A diluted with 20 cc of 60/80 mesh silicon carbide particles placed on top of 20 cc of Catalyst B diluted with 20 cc of 60/80 mesh silicon carbide particles. The catalysts were presulphided in the reactor by heating them to about 371 °C and holding at such temperature for about two hours in a 95 vol.% hydrogen-5 vol.% hydrogen sulphide atmosphere flowing at a rate of about 60 litres/hour.

After catalyst presulphidization, the catalyst beds were stabilized by passing the feedstock from Table 2 with its sulphur content adjusted to 1600 ppm by the addition of benzothiophene over the catalyst bed for over about 48 hours at about 316 °C at a system pressure of about 102 bar and a liquid volume hourly

space velocity of about 1 hour⁻¹. Hydrogen gas was supplied on a once-through basis at a rate of about 535 vol/vol. The reactor temperature was gradually increased to about 332 °C and allowed to stabilize. During this period, spot samples were collected daily and analyzed for refractive index ("RI"). The catalyst(s) was considered to have stabilized once product RI was stable.

During the course of this study, sulphur contents of the feedstock were adjusted by adding suitable amounts of benzothiophene and reactor temperature, system pressure, LHSV, and hydrogen gas rate were adjusted to the conditions indicated in Tables 3, 4 and 5. Product liquid samples were collected at each process condition and analyzed for S, N, and aromatics (by fluorescent indicator adsorption technique ("FIA"); ASTM D-1319-84). These results are shown in Tables 3, 4 and 5.

TABLE 3: CATALYST BED CONTAINING CATALYST A

Run No.	S in Feed, ppm	Cat. Age, hr.	LHSV, hr ⁻¹	Run Temp., °C	Total Press., bar	Gas Rate, vol/vol	Product N, ppm	Product S, ppm	FIA ²⁾ Conv.
A1	1600	2110	1.00	371	102	535	-	1.0	61.1
A2	1600	2591	1.01	371	102	535	1.0	1.0	67.1
A3	1600	3024	1.00	371	102	535	-	-	66.4
A4	1600	3672	0.98	371	75	535	-	5.0	25.0
A5	1600	3814	1.01	371	48	535	-	37.0	-2.9
A6	10,350	3560	1.00	371	102	535	1.0	6.0	38.7

1) Catalyst age represents the time that the catalyst bed has been operated since it reached temperature of 204 °C.

2) % aromatics conversion by FIA (ASTM D-1319-84).

Conversion defined as Vol.% FIA content of feed - Vol.% FIA content of product
Vol.% FIA content of feed

TABLE 4: CATALYST BED CONTAINING CATALYST B

Run No.	S in Feed, ppm	Cat. ¹⁾ Age, hr.	LHSV hr ⁻¹	Run Temp. °C	Total Press. bar	Gas Rate vol/vol	Product		FIA ²⁾ Conv.
							N, ppm	S, ppm	
B1	1600	384	1.00	371	75	535	1.0	2.2	26.7
B2	1600	462	0.99	371	48	535	16.0	7.9	-1.2
B3	1600	503	1.01	371	102	535	1.0	2.0	36.5
B4	10,350	631	1.02	371	102	535	<1	3.5	52.9
B5	10,350	647	1.02	371	102	535	<1	2.3	53.3

1) Catalyst age represents the time that the catalyst bed has been operated since it reached temperature of 204 °C.

2) % aromatics conversion by FIA (ASTM D-1319-84).

Conversion defined as Vol.% FIA content of feed - Vol.% FIA content of product

Vol.% FIA content of feed

TABLE 5: CATALYST BED CONTAINING CATALYST A ON TOP OF CATALYST B

Run No.	S in Feed, ppm	Cat. Age, hr.	LHSV, hr ⁻¹	Run Temp., °C	Total Press., bar	Gas Rate, vol/vol	Product N, ppm	Product S, ppm	FIA ²⁾ Conv.
A/B1	1600	330	0.99	371	102	535	<1	<1	58.6
A/B2	1600	489	1.00	371	102	535	<1	12	63.0
A/B3	1600	561	1.00	371	75	535	5	11	40.9
A/B4	1600	657	1.01	371	48	535	25	20	2.1
A/B5	1600	848	0.39	371	48	535	<1	7	14.9
A/B6	1600	978	0.98	371	102	535	1	14	51.2
A/B7	10,350	1148	1.01	371	102	535	<1	14	49.2
A/B8	10,350	1170	1.02	371	102	535	<1	17	50.6
A/B9	10,350	1216	0.99	371	75	535	2	20	26.5
A/B10	10,350	1264	1.02	371	48	535	19	28	9.9
A/B11	10,350	1314	0.36	371	48	535	1	22	30.5
A/B12	10,350	1362	1.00	371	102	535	<1	20	48.2
A/B13	1600	1416	0.97	371	102	535	<1	19	61.6

1) Catalyst age represents the time that the catalyst bed has been operated since it reached temperature of 204 °C.

2) % aromatics conversion by FIA (ASTM D-1319-84).

Conversion defined as Vol.% FIA content of feed - Vol.% FIA content of product
Vol.% FIA content of feed

As can be seen from the above data, the present invention provides for enhanced aromatics saturation over Catalyst A at high sulphur levels and over Catalyst B at low sulphur levels.

Claims

1. A process for the concomitant hydrogenation of aromatics and sulphur-bearing hydrocarbons in an aromatics- and sulphur-bearing hydrocarbon feedstock having substantially all of its components boiling in the range of 93 to 482 °C which process comprises:
 - (a) contacting at a temperature between 315 and 399 °C and a pressure between 40 and 168 bar in the presence of added hydrogen said feedstock with a first catalyst bed containing a hydrotreating catalyst comprising nickel and tungsten supported on an alumina support, and
 - (b) passing the hydrogen and feedstock without modification, from the first catalyst bed to a second catalyst bed where it is contacted at a temperature between 315 and 399 °C and a pressure between 40 and 168 bar with a hydrotreating catalyst comprising a hydrogenating metal component selected from cobalt, nickel and mixtures thereof and molybdenum supported on an alumina

support.

2. The process of claim 1 wherein the support for the catalyst in the first catalyst bed has a surface area greater than 100 m²/g and a water pore volume ranging from 0.2 to 0.6 cc/g and the support for the catalyst in the second catalyst bed has a surface area greater than 120 m²/g and a water pore volume ranging from 0.2 to 0.6 cc/g.
3. The process of claim 1 and/or 2 wherein in the catalyst in the first bed the nickel content ranges from 1 to 5 percent by weight of the total catalyst, measured as the metal and the tungsten content ranges from 15 to 35 percent by weight of the total catalyst, measured as the metal and wherein in the catalyst in the second bed the hydrogenating metal component content ranges from 1 to 5 percent by weight of the total catalyst, measured as the metal and the molybdenum content ranges from 8 to 20 percent by weight of the total catalyst, measured as the metal.
4. The process of any one of claims 1-3 wherein the sulphur content of the feedstock ranges from 0.01 to 2 percent by weight.
5. The process of claim 4 wherein the sulphur content of the feedstock ranges from 0.05 to 1.5 percent by weight.
6. The process of any one of claims 3-5 wherein in the catalyst in the first bed the nickel content ranges from 2 to 4 percent by weight of the total catalyst, measured as the metal and the tungsten content ranges from 20 to 30 percent by weight of the total catalyst, measured as the metal and wherein in the catalyst in the second bed the hydrogenating metal component content ranges from 2 to 4 percent by weight of the total catalyst, measured as the metal and the molybdenum content ranges from 12 to 16 percent by weight of the total catalyst, measured as the metal.
7. The process of any one of claims 1-6 wherein the hydrogenation of the feedstock takes place at a hydrogen partial pressure ranging from 35 to 149 bar, feedstock is provided at a liquid hourly space velocity ranging from 0.1 to 5 hour⁻¹ and added hydrogen is provided at a feed rate ranging from 178 to 891 vol/vol.
8. The process of any one of claims 1-7 wherein the catalyst selected from the catalyst in the first catalyst bed, the catalyst in the second catalyst bed and the catalyst in both the first and second catalyst beds additionally comprises phosphorous.
9. The process of claim 8 wherein in the catalyst in the first bed the nickel content ranges from 1 to 5 percent by weight of the total catalyst, measured as the metal; the tungsten content ranges from 15 to 35 percent by weight of the total catalyst, measured as the metal, and the phosphorous content ranges from 1 to 5 percent by weight of the total catalyst, measured as the element and wherein in the catalyst in the second bed the hydrogenating metal component content ranges from 1 to 5 percent by weight of the total catalyst, measured as the metal; the molybdenum content ranges from 8 to 20 percent by weight of the total catalyst, measured as the metal, and the phosphorous content ranges from 1 to 5 percent by weight of the total catalyst, measured as the element.
10. The process of claim 9 wherein in the catalyst in the first bed the nickel content ranges from 2 to 4 percent by weight of the total catalyst, measured as the metal; the tungsten content ranges from 20 to 30 percent by weight of the total catalyst, measured as the metal; and the phosphorous content ranges from 2 to 4 percent by weight of the total catalyst, measured as the element and wherein in the catalyst in the second bed the hydrogenating metal component content ranges from 2 to 4 percent by weight of the total catalyst, measured as the metal; the molybdenum content ranges from 12 to 16 percent by weight of the total catalyst, measured as the metal and the phosphorous content ranges from 2 to 4 percent by weight of the total catalyst, measured as the element.



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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 1649

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	FR-A-1 281 534 (BP)abstract 1-12 ---	1-7	C 10 G 65/08
Y	US-A-4 619 759 (MYERS ET AL) * column 4, line 23 - line 53; claims 1-12 *	1-7	
D,A	US-A-4 530 911 (RYAN ET AL) * claims 1-11 *	8-10	
D,A	US-A-4 520 128 (MORALES ET AL) * claims 1-16 *	8-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		08 October 91	MICHIELS P.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document			